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TITLE: THERMOSETTING ADHESIVE COMPOSITION
(Netsukokasei settyakuzai soseibutsu)

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[note: All names, addresses, company names, and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. translator's note]

As for the conventional adhesive agents used in these applications to adhere films such as polyester or polyimide and copper foil, it includes such types which are prepared by coating resin solution of combination of epoxy resin, phenol resin, nitrile rubber, butylal resin, and nylon, or polyamide acid or polyamide imide dissolved in solvent on a substrate film through use of roll coater and the like, and then, it is heat dried in with a dryer to semi-harden the adhesive agent to B state, and head press adhering this with a copper foil to give copper plate sheet for flexible printed circuit wiring purpose, or to be used as an overlay film as it is.

On the one hand, when forming a composite material as a film, it may be done by impregnating resin solution same as those explained above on a reinforcement substrate such as glass cloth or polyamide nonwoven cloth to be used in the same manner as explained above.

However, according to above-explained methods, as goods of rubber group are added to provide flexibility, it presents problem of miscibility with resin, and even then, it shows a defect of weak peel strength compared to shear strength due to lack of flexibility. In addition, resin solution of polyamide acid or polyamide imide is not only costly, but also it generates gas during heating and pressing. Furthermore, when this is viewed from the standpoint of production technologies, in order to dissolve above-explained resins, it is necessary to use large amount of polar solvents which are difficult to evaporate to require a large volume of energy as well as long and large drying oven for heat drying after said coating. And therefore, these conventional methods are not only uneconomical, but also present large problems from the standpoint of safety hygiene as well as hazard prevention; and these factors cause significant affect on reduction in production speed.

[Problem points solved by this invention]

Based on above-explained defects of conventional technologies, this invention was completed after various studies; and its purpose is to offer a non-solvent type resin composition that can provide a B stage thermosetting adhesive agent instantly through irradiation of electrolytic radiation ray. That is to say, according to this invention, said resin composition comprises low molecular weight urethane acrylate, epoxy resin, acrylate or methacrylate monomer, and epoxy curing agent to provide an adhesive agent showing good miscibility , excellent flexibility not seen in physical properties of adhesive agents prepared by heating and press adhesion, and excellent adhesion to film substrate as well as good physical properties including heat resistance and electrical properties.

On the one hand, as for the di and triol, polyether polyol or polyester polyol used for production of general polyurethane may be mentioned. As for the polyether polyol, polyethylene glycol or polypropylene glycol of which ethylene oxide or propylene oxide is opened polymerized may be mentioned.

As for the polyester polyol, Jarubonic [transliteration] acid to which polyhydric alcohol is condensed to convert its terminal to OH, polymerized lactone glycol ester, or castor oil may be mentioned. In addition, polybutadiene of which both terminals are of hydroxyl group or carboxyl group is also useful. These polyols may be used as a mixture of more than two types.

In addition, acrylate compound has at the least one hydroxyl group or carboxyl group within one molecule; and concrete examples include hydroxy ethyl acrylate, hydroxy propyl acrylate, hydroxy butyl acrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate, hydroxy butyl methacrylate, 4-hydroxy cyclohexyl acrylate, 5-hydroxy cyclo octyl acrylate, 5-hydroxy cyclooctyl acrylate, 2-hydroxy-3-phenyloxy propyl acrylate, acrylic acid, methacrylic acid; or compounds containing one active hydroxyl group such as adducts of 2-hydroxy ethyl acrylate and phthalic anhydride.

Furthermore, as for the acrylate compound that is the starting raw material, addition reaction products of diepoxy compounds and acrylic acid such as ethylene glycol diglycidyl ether dimethacrylate, diethylene glycol diglycidyl ether dimethacrylate, propylene glycol diglycidyl ether diacrylate, phthalic acid diglycidyl ester diacrylate; or reaction product of glycidyl (meth)acrylate and dibasic acid may be mentioned; and at this time, dibasic acid includes itaconic acid, maleic acid, fumaric acid, succinic acid, adipic acid, and terephthalic acid.

The reaction of these components may be carried out under ordinary reaction conditions in following manner:

(1) Straight chain urethane compound is produced by reacting excess diisocyanate with diol to form a prepolymer having isocyanate group at two terminals at the least, and then, acrylate compound having hydroxy group or carboxyl group is reacted with both terminals.

As for the acrylate monomer that is the third component of this invention, for instance, various ester acrylates such as ethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, 1,6-hexane diol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, dipropylene glycol diacrylate, dipentaerithritol penta acrylate, dipenta erithritol hexa acrylate, diethyl amino ethyl acrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethyl hexyl acrylate, isodecyl acrylate, lauryl acrylate, stearyl acrylate, 2-hydroxy ethyl acrylate, 2-hydroxy propyl acrylate, trimethylol propane triacrylate, methoxy ethyl acrylate, n-butoxy ethyl acrylate, tetrahydro furfuryl acrylate, glycidyl acrylate, ethyl carbitol acrylate, methyl triglycol acrylate, benzyl acrylate, 1,5-pentane diol diacrylate, pentaerithritol triacrylate, and 2-hydroxy ethyl acryloyl phosphate as well as corresponding ester methacrylates may be used; and they may be used either alone or as more than two types.

These are polymerized and cured along with said polyurethane while leaving epoxy groups through electrolytic radiation ray to not only form tack free prepreg, but also contributes toward adjustment of viscosity of resin solution and adhesive features of substrate and adherend; and in addition, they also serve a function of adjusting resin flow during heating and press adhesion. These may be used at 20 to 400 parts by weight based on 100 parts by weight first component; and when it happens to be less than 20 parts by weight, pressure-sensitive adhesive features of prepreg cannot be solved sufficiently nor viscosity can be reduced; and when it happens to exceed 400 parts by weight, performance as an adhesive agent declines.

As for the last fourth component of epoxy curing agent, one or more than two types of aliphatic amine group, aromatic amine group, cyclic aliphatic amine group, acid anhydride group, dicyan amide, boron trifluoride complex compound may be used; and it is recommended to use aromatic amine group and acid anhydride group from the standpoint of improved heat resistance and electrical insulation property; and it may be added at appropriate amount according to compounding of resin solution.

As for the electrolytic radiation ray, X-ray, gamma-ray, and electron beam may be used; and electron beam is recommended from the standpoint of large transmissivity and possible high speed treatment; and in the case of electron beam, electron beams with 50 to 100 KeV or more preferably, 100 to 300 KeV range energy discharged from various electron beam accelerators including Cockcroft-Walton accelerator, van de Graff accelerator, resonance transformation type, insulation core transformation type, linear type, dynatron type, and high frequency type may be used. As for the irradiation dosage, 1 to 50 Mrad may be used; and when it happens to be less than 1 Mrad, curing remains insufficient and pressure-sensitive adhesive features remain; and when it happens to exceed 50 Mrad, curing progresses too much to inhibit flowability and adhesive features of resin. Although it depends on the composition, irradiation dosage of electron beam show significant affect on crosslinking density; and 3 to 20 Mrad is recommended from the standpoint of adhesive features and heat resistance.

In addition, it is necessary to avoid contact with film and reinforcement substrate that is either coated or impregnated with resin solution during handling; and above all, even after preliminary curing through electron beam irradiation, tack may remain on the surface to require releasable film and the like when this is piled; and in addition, due to tack on the surface, dust and the like tends to adhere easily. In order to prevent from those hindrance, it is recommended to adhere releasable film with a laminator and the like after coating and impregnating resin solution on heat resistant film and reinforcement substrate; and said releasable film includes, for instance, general films such as polyvinylidene chloride, polyvinyl chloride, ethylene/vinyl acetate copolymer, polytetrafluoro ethylene, polystyrene, polyethylene, polypropylene, polymethyl methacrylate, polyethylene terephthalate, polycarbonate, or polyamide; and 12 to 100 μm thickness is recommended. Even when above-explained film is adhered to either one plane or both planes of reinforcement substrate prepared through coating and impregnation of resin solution, effect of irradiation of electron beam is not substantially reduced; and as it is blocked from oxygen in air through close adhesion of film, it is not controlled with curing by oxygen in air during electron beam irradiation to allow effective preliminary curing.

EXAMPLE 2

A prepolymer having isocyanate group at both terminals was prepared in the same manner as explained in the example 1 by dropping 1200 g polyethylene glycol (200 molecular weight) in 1500 g xylilene diisocyanate and 1.1 g dibutyl tin dilaurate.

219 g hydroxyethyl acrylate was further dropped in above given prepolymer to give a prepolymer having isocyanate group at its one terminal and acryl group at the other.

Furthermore, 450 g triol (3,000 molecular weight) of polypropylene glycol was dropped in above-explained prepolymer having isocyanate group and acryl group at 50°C reaction temperature; and after dropping was completed, 1.3 g hydroquinone was added, and this was continued to react for 3 hours while maintaining the temperature at 50°C to give an electrolytic radiation ray curable urethane resin (B).

This urethane resin was used; and was compounded at following compounding ratio to give an adhesive composition:

electrolytic radiation curable urethane resin (B)	100 parts by weight
epoxy resin (Epikote 815 made by Shell Chemical Co.)	60 parts by weight
2-hydroxy-3-phenoxy propyl acrylate	100 parts by weight
metaphenylene diamine	15 parts by weight

This composition was used to prepare a prepreg in the same manner as explained in the example 1. Adhesion conditions of this prepreg and flexible printed circuit board were 120°C, 10 kg/cm^3, and 1 hour; and it showed following physical properties:

	testing method	numeral value
peel strength	90° peeling	1300 g/cm
bend resistance strength	JIS-P-8115	more than 1000 x
solder heat resistance	JIS-C-6481	no abnormality